

Uranyl Salts

International Edition: DOI: 10.1002/anie.201609838 German Edition: DOI: 10.1002/ange.201609838

Facile Reductive Silylation of UO₂²⁺ to Uranium(IV) Chloride

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Abstract: General reductive silvlation of the UO_2^{2+} cation occurs readily in a one-pot, two-step stoichiometric reaction at room temperature to form uranium(IV) siloxides. Addition of two equivalents of an alkylating reagent to $UO_2X_2(L)_2$ (X = Cl, Br, I, OTf; L = triphenylphosphine oxide, 2,2'-bipyridyl) followed by two equivalents of a silvl (pseudo)halide, R_3Si-X (R = aryl, alkyl, H; X = Cl, Br, I, OTf, SPh), cleanly affords ($R_3SiO_2UX_2(L)_2$ in high yields. Support is included for the key step in the process, reduction of U^{VI} to U^V . This procedure is applicable to a wide range of commercially available uranyl salts, silvl halides, and alkylating reagents. Under this protocol, one equivalent of $SiCl_4$ or two equivalents of Me_2SiCl_2 results in direct conversion of the uranyl to uranium(IV) tetrachloride. Full spectroscopic and structural characterization of the siloxide products is reported.

he ubiquity of the uranyl cation $[UO_2]^{2+}$ is due in part to the robust nature of the *trans*-dioxo moiety,^[1] which renders these moieties resistant to activation or functionalization.^[2] The persistence of these uranium(VI) species in nature is problematic due to their high water solubility and subsequent mobility; however, reduction to tetravalent species through pentavalent $[UO_2]^+$ intermediates in anaerobic conditions can mitigate this on account of the poor solubility of lower valent forms.^[1] Though studied using a variety of methods,^[2] including electrochemically^[3] and photochemically,^[4] a fruitful strategy for U=O reduction is reductive silvlation, where the driving force is formation of O-Si bonds. Previous reductive silvlation systems are limited by the need for large excesses of silvl halides,^[5-7] side reactivity of coordinated ligands^[5,6] or their use as sacrificial reductants,^[8] the need for pre-activation,^[9-11] or the requirement of complex macrocyclic ligands.^[12] Our progress in reductive silylation has suffered from similar flaws. We recently reported a novel uranyl species, $[Cp*UO_2(^{Mes}PDI^{Me})]$ (Cp* = 1,2,3,4,5-penta-methylcyclopentadienide, $^{Mes}PDI^{Me} = 2,6$ -((Mes)N=CMe)₂- C_5H_3N , Mes = 2,4,6-trimethylphenyl), bound by a redox active pyridine(diimine) ligand. While formally uranium(V), this complex is best described spectroscopically as a uranium-(VI) ion bound by a mono(anionic) [MesPDI^{Me}]^{1-.[13]} Using a Lewis base to pre-activate the silvl halide facilitates stoichiometric reductive silvlation at room temperature,

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which is accompanied by a reduction from U^{VI} to $U^{IV,[8]}$ However, the reducing electrons are derived from the Cp* and ^{Mes}PDI^{Me} ligands, which are subsequently lost. Thus, a more general, commonly available electron source was targeted.



M-R = KCH₂Ph, ⁿBuLi, MCH₂SiMe₃ (M = Li, Na, K)

In organometallic chemistry, two electrons can be conveniently accessed through reductive elimination; we hypothesized that carbon-carbon reductive elimination from a uranyl dialkyl species would serve as an effective electron source to facilitate reductive silvlation of the transdioxo moiety. Pioneering work by Seyam and co-workers described the synthesis of a family of thermally unstable uranyl dialkyls of the type UO_2R_2 (R = Me, vinyl, ^{*i*}Pr, ^{*n*}Bu, ^tBu, Ph) from the metathesis of [UO₂Cl₂] with alkylation reagents.^[14] While the organometallic uranyls eluded isolation, the organic byproducts formed upon warming were derived through: 1) H-atom abstraction, 2) β-hydride elimination, and 3) reductive elimination (R = Ph only). Subsequently, the first uranyl alkyl complex, [Li(DME)_{1.5}]₂[UO₂- $(CH_2SiMe_3)_4$], has been isolated and characterized by Hayton et al.[15]

To test this theory, a thawing THF slurry of [UO₂Cl₂- $(OPPh_3)_2$] (1) was treated with 2 equiv NaCH₂SiMe₃, causing an immediate color change from yellow to light brown. After ca. 30 seconds of stirring, two equivalents of Me₃SiCl were added, and the solution was warmed to room temperature, resulting in bleaching of the solution, affording $[(Me_3SiO)_2UCl_2(OPPh_3)_2]$ (2) [Eq. (1)] as determined by ¹H NMR spectroscopy and X-ray crystallography (Figure 1; Table S1 in the Supporting Information). 2 adopts a pseudooctahedral geometry with cis-chlorides (94.71(3)°), comparable to the structure of [cis-(Ph₃PO)₂UCl₄],^[16] but dissimilar to its heavier halide analogues.^[8] Consistent with the instability described by Seyam, addition of Me₃SiCl to the uranyl/ metalalkyl mixture after greater than 30 seconds resulted in lower yields with inseparable byproducts. Notably, employment of four equiv of Me₃SiCl did not result in full oxo-ligand cleavage-consistent with previous observations from our lab.

A screen of commonly available alkylating reagents demonstrated that similar yields of **2** were obtained for MCH₂SiMe₃ (M = Li, Na, K), "BuLi, and KCH₂Ph. For "BuLi, NaCH₂SiMe₃, and KCH₂C₆H₅, the reductive elimination products (C₈H₁₈, Me₃SiCH₂CH₂SiMe₃, and PhCH₂CH₂Ph, respectively) were observed by ¹H NMR spectroscopy and/

Angew. Chem. Int. Ed. 2016, 55, 1-5

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Figure 1. Molecular structure of **2** displayed with 30% probability ellipsoids. Phenyl substituents, H atoms, and co-crystallized solvents have been omitted for clarity. Select bond lengths (Å) and angles: U1–O1 2.1267(18), U1–O3 2.3620(17), U1–Cl1 2.6800(7); O1-U1-O2 173.56(7)°, Cl1-U1-Cl2 94.71(3)°.

or GC/MS. Crossover experiments suggested a radical mechanism (see the Supporting Information). Formation of **2** was not observed when NaBHEt₃ or MeMgX (X = Cl, Br) were used. Overall, MCH₂SiMe₃ reagents generally afforded the cleanest products. To facilitate salt separation, NaCH₂SiMe₃ was employed for subsequent work over the commercially available LiCH₂SiMe₃.

In situ alkylation of the uranyl allows for a wide variety of silyl reagents (Table 1), including R_3Si -Cl reagents where R = Me, Et, Ph or H. Treatment of **1** with two equiv of $NaCH_2SiMe_3$ followed by two equiv of R_3Si -Cl cleanly generates $[(R_3SiO)_2UCl_2(OPPh_3)_2]$ ($R_3 = Me_3$; Et₃ (**3**) Me_2Ph ; $MePh_2$; Ph_2H (**4**)) in high yields after work up. The silylation with Me_3SiCl was repeated in the dark and afforded **2** in 61% isolated yield suggesting the reaction is not photochemically induced. As for other reductive silylation systems, bulky silyl-halides do not produce clean reactions. For example, although Ph_3Si -Cl proceeds with respectable silylated yields, it does so more slowly with unidentified and inseparable byproducts, as previously noted.^[8,16] Not surprisingly, the most sterically encumbered reagent, ^{*i*}Pr_3Si-Cl, does not reductively silylate, consistent with the inability of the oxo

Table 1: Scope of silulating reagents for reductive silulation of UO_2^{2+} (1).

O Ph ₃ PO ₁₂ , [] CI U O OPPh ₃ 1	$\frac{1) 2 \text{ NaCH}_2 \text{SiMe}_3}{\text{THF, -108 °C, 30 so}} \\ \frac{2) 2 \text{ R}_3 \text{Si-X}}{\text{THF, RT, 1 hr}}$	ec F	$\begin{array}{c} \text{R}_3\text{Si-O} \\ \text{X}_{\text{M}_2} \\ \text{Ph}_3\text{PO} \\ \text{O} \\ \text{SiR}_3 \end{array} + 2 \text{ NaCl} \\ + \text{Me}_3\text{SiCH}_2\text{CH}_2\text{SiMe}_3 \\ \text{SiR}_3 \end{array}$
R₃Si-X	$Yield \ [\%]^{^{[a]}}$	Х	Product
Me₃Si-Cl	73	Cl	2
Et₃Si-Cl	72	Cl	3
Me ₂ PhSi-Cl	82	Cl	[(Me ₂ PhSiO) ₂ UCl ₂ (OPPh ₃) ₂]
MePh ₂ Si-Cl	87	Cl	[(MePh ₂ SiO) ₂ UCl ₂ (OPPh ₃) ₂]
Ph₂HSi-Cl	76	Cl	4
Ph ₃ Si-Cl	63 ^[b]	Cl	[(Ph ₃ SiO) ₂ UCl ₂ (OPPh ₃) ₂]
iPr₃Si-Cl	0	Cl	_
Me₃Si-SPh	80	SPh	$[(Me_3SiO)_2U(SPh)_2(OPPh_3)_2]$

[a] Yields of isolated products. [b] Yield determined by ¹H NMR spectroscopy.

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moiety to perform nucleophilic attack on the protected silicon atom.^[17] In the case of $Me_3Si-SPh$, the bis(thiophenolate) species, $[(Me_3SiO)_2U(SPh)_2(OPPh_3)_2]$, is formed without anion metathesis (see below).

While Lewis base adducts of uranyl chloride are common, we sought to extend this reductive silylation strategy to other uranyls (Table 2). Reductive silylation of $[UO_2X_2(OPPh_3)_2]$

Table 2: Reductive silylation of uranyl complexes.

$\begin{array}{c} O \\ L_{II_{0}} \prod_{i=1}^{N} (X) \\ X \prod_{i=1}^{N} (L)_{n} \end{array} \xrightarrow{\begin{array}{c} 1 \\ THF, -10 \\ 2 \\ THI \end{array}} $	CH ₂ SiMe ₃ 8 °C, 30 sec 2 Me ₃ Si-X F, RT, 1 hr	Me ₃ Si	$ \begin{array}{c} & & \\ & & $
Uranyl	Yield [%] ^[a]	Х	Product
$UO_2I_2(OPPh_3)_2$	80 ^[b]	l	$[(Me_3SiO)_2UI_2(OPPh_3)_2]$ 2
$UO_2CI_2(OPPh_3)_2$ (1)	73	Cl	
UO ₂ Br ₂ (OPPh ₃) ₂	75	Br	[(Me ₃ SiO) ₂ UBr ₂ (OPPh ₃) ₂]
UO ₂ (OTf) ₂ (2,2'-bpy) ₂	87	OTf	5
[UO ₂ (OPPh ₃) ₄][OTf] ₂	5 ^[c]	OTf	[(Me ₃ SiO) ₂ U(OTf) ₂ (OPPh ₃) ₂]

[a] Yields of isolated products. [b] Reaction in 1,4-dioxane. [c] Yield determined by 1 H NMR spectroscopy.

(X = Br, I) proceeds in high yields, generating $[(Me_3SiO)_2UX_2(OPPh_3)_2]$. We noted that if the halide of the silyl reagent employed is different than the uranyl salt, halide scrambling is observed due to back-reaction of the NaX byproduct. For example, reductive silylation of $[UO_2I_2(OPPh_3)_2]$ with Me₃Si-Br results in an inseparable mixture of $[(Me_3SiO)UI_xBr_y(OPPh_3)_2]$ (x + y = 2) (see the Supporting Information). To cease "X" ligand scrambling, the halides on the silane and uranyl were matched. Judicious solvent choice is also important; deleterious reductive ring opening of THF, detected by formation of $I(CH_2)_4OSiMe_3$ (Figure S18), was prevented in the reductive silylation of $[UO_2I_2(OPPh_3)_2]$ using 1,4-dioxane.

Surprisingly, attempts at reductive silvlation of [UO₂-(OPPh₃)₄][OTf]₂ have been unsuccessful under this protocol, with only trace $[(Me_3SiO)_2U(OTf)_2(OPPh_3)_2]$ observed by ¹H NMR spectroscopy, despite success by Hayton with similar species.^[18] This is notable since reductive silylation of [UO₂- $(OTf)_2(2,2'-bpy)_2$] (bpy = bipyridyl)^[19] proceeds to give $[(Me_3SiO)_2U(OTf)_2(2,2'-bpy)_2]$ (5) in high yields, suggesting triflate is not an inherently poor anion choice. We hypothesized the decreased reactivity of [UO₂(OPPh₃)₄][OTf]₂ towards reductive silvlation stemmed from its high reduction potential. Notably, replacement of NaCH₂SiMe₃ in the reaction with two equiv of KC8 gives only a slightly increased yield (27%). Since pentavalent uranyl, UO_2^+ , has heightened Lewis basicity as compared to its oxidized counterpart, it is often invoked as a key intermediate in such processes. As a consequence, a UO2⁺ moiety should display increased reactivity toward electrophilic silanes. Electrochemical analysis of [UO₂(OTf)₂(2,2'-bpy)₂] displayed a single electron reduction at -2.108 V vs. Fc/Fc⁺, but no redox events were observed for $[UO_2(OPPh_3)_4][OTf]_2$ in the experimental window (MeCN, 0.1M [Bu₄N][OTf]) (Figure S20). This result is consistent with findings by Ephritikhine,^[20] but contrasts those of Duval, who reports an irreversible wave (0.1M $[Bu_4N][PF_6]$).^[3] These data highlight initial reduction to uranium(V) is essential for facile reductive silylation. We propose in this work the first equivalent of NaCH₂SiMe₃ is likely responsible for the UO₂²⁺/UO₂⁺ reduction, as was previously noted by Ephritikhine for the reduction of UO₂OTf₂ with LiCH₂SiMe₃.^[21]

To probe the plausibility of a uranium(V) reaction pathway for the reductive silylation of UO_2^{2+} , the pentavalent intermediate was generated in situ, and its reactivity tested. Rather than using the standard alkylation procedure, reduction of **1** was performed first with one equiv KC₈, followed by stirring for one hour. This generated the pentavalent uranyl intermediate, "[UO₂Cl(OPPh₃)₂]", which was then alkylated with NaCH₂SiMe₃ and reductively silylated with Me₃SiCl to cleanly afford **2** (64%, Figure S19) [Eq. (2)]. Replacement of the alkylating agent by heterogeneous reductant (two equiv of KC₈) also produced **2**, albeit in significantly lower yields (38%).

Performing the alkylation and silylation of **1** with only one equiv each of NaCH₂SiMe₃ and Me₃SiCl affords **2** in 44% yield as well as starting material, **1** (32% yield), as confirmed by IR spectroscopy [Eq. (3)]. While this suggests only one-





half of the starting material is converted in the reaction, it is also plausible that all of **1** is reduced, and upon silylation, forms a putative mono-silylated species, $[(Me_3SiO)UOCl_2-(OPPh_3)_2]$. This species may rapidly disproportionate via oxo ligand scrambling^[22] or silyl radical transfer^[23] to form half an equiv each of **1** and **2**. Silylation of a single oxo moiety of uranyl has previously been proposed by our lab^[13] and others,^[10] and has been elegantly captured through the use of polypyrrolic macrocycles by Arnold et al.^[12]

Spectroscopically, the reductive silvlation products share similar features. For each complex, ¹H NMR spectroscopic analysis revealed downfield shifted resonances for trans-OSiR₃ protons, with the Ph₂HSi- proton of 4 the most affected (107.35 ppm, C_6D_6 , Figure S16). The resonances for protons in the equatorial plane (OPPh3 or 2,2'-bpy) are the most upfield shifted and consistent with data for similar compounds.^[8] Neither ²⁹Si nor ³¹P resonances were observable. By IR spectroscopy, complexes bearing OPPh₃ showed P=O stretches consistent with the literature ($v_{(P=O)}$: 1077– 1073 cm⁻¹), regardless of oxidation state.^[24] The electronic absorption spectra of the silvlated species all display sharp, weakly intense transitions in the near IR region indicative of uranium(IV) ions (Figure S9). The halide species all display UV absorptions with the energy of this transition following the trend Cl > Br > I > SPh; the triflate species does not absorb in the experimental window.

Single crystal X-ray diffraction studies of **3**, **4**, and **5** were performed to establish their molecular structures (Figure 2, Table S1). All complexes possess *trans*-siloxide ligands (U– OSiR₃ = 2.09–2.19 Å) that are significantly elongated from their uranyl counterparts,^[19,24] but are on par with other uranium(IV) siloxides.^[25] Not uncharacteristic of the poor binding capabilities of triflates, the neutral phosphine oxide ligands of **4** (U–OPPh_{3(ave)} = 2.29 Å) bind the uranium significantly stronger than the triflates of **5** (U–OTf_(ave) = 2.43 Å). The siloxide ligands of eight coordinate **5** deviate



Figure 2. Molecular structures of 3 (left), 4 (middle), and 5 (right) displayed with 30% probability ellipsoids. Select phenyl substituents, H atoms, and co-crystallized solvents have been omitted for clarity. Select bond lengths (Å) and angles of 3: U1–O1 2.107(2), U1–O3 2.3509(19), U1–Cl1 2.6800(7); O1-U1-O2 173.56(7)°, Cl1-U1-Cl2 94.47(3)°. 4: U1–O1 2.120(5), U1–O3 2.299(5), U1–Cl1 2.6795(8); O1-U1-O2 174.56(9)°, Cl1-U1-Cl2 175.17(7)°. 5: U1–O1 2.115(13), U1–O3 2.444(11), U1–N1 2.662(15), U1–N2 2.679(16); O1-U1-O2 155.5(5)°, O3-U1-O4 153.3(4)°.

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most from linearity (O1-U-O2=155.5(5)°); however, this angle is far more linear as compared to $[(Me_3SiO)_2UI_2(2,2'-bpy)_2]$ (115.5(2) Å).^[5]

With spectroscopic, structural, and mechanistic insight into uranyl reductive silylation, we aimed to extend our alkylation strategy. Full oxo-cleavage of **1** was achieved using 2 equiv each of NaCH₂SiMe₃ and Me₂SiCl₂ sequentially forming [(Ph₃PO)₂UCl₄], presumably via β-chloride elimination from [(ClMe₂SiO)₂UCl₂(OPPh₃)₂] [Eq. (4); Figures S1 and S2), along with (Me₂SiO)_n (n = 6, 8, 10, 12) as confirmed by GC/MS. Similarly, using one equivalent of SiCl₄ affords [(Ph₃PO)₂UCl₄] (confirmed by X-ray crystallography, IR and NMR; Figures S3–S5) in high yields with extrusion of amorphous SiO₂ (identified by IR spectroscopy) [Eq. (5)]. Thus, choice of silylating reagent plays a key role in the bond scission.



In summary, we have described a general methodology for the stoichiometric reductive silylation of common uranyl starting materials, by employing commercially available alkylating reagents for the in situ formation of uranyl alkyls. These elusive species show unprecedented reactivity toward silyl halides to form uranium(IV) disiloxides in high yields by silylation of a transient uranium(V) alkyl complex. Future work will be aimed at examining the role uranium(V) plays in reductive silylation as well as at extending this protocol to other sources of electrophiles.

Acknowledgements

We gratefully acknowledge Prof. Nathaniel K. Szymczak and his group for helpful discussions, as well as funding from the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences of the U.S. Department of Energy through Grant DE-SC0008479. The X-ray diffractometer was funded by NSF Grant DMR 1337296.

Conflict of interest

The authors declare no conflict of interest.

Keywords: alkylation · oxo complexes · reduction · reductive silylation · uranium

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Manuscript received: October 7, 2016 Revised: November 19, 2016 Final Article published:



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Communications

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Facile Reductive Silylation of UO₂²⁺ to Uranium(IV) Chloride



The persistence of uranium(VI) species in nature is problematic due to their high water solubility and subsequent mobility. A general methodology for the stoichiometric reductive silylation of common uranyl(VI) salts under mild conditions allows for direct conversion of UO_2^{2+} to uranium(IV) chloride through the use of SiCl₄.